INDUSTRIAL EXPERIENCE

UDC 666.11.019.17:666.151.004.18

CAUSES OF GLASS MELT TINTING WHEN EMPLOYING CULLET IN MAXIMUM QUANTITY

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Translated from Steklo i Keramika, No. 7, pp. 30 – 32, July, 1999.

The bulk tinting of glass produced using the maximum amount of cullet is investigated. The possibility of producing industrial quantities of glass for construction purposes using glass waste is demonstrated, which ensures significant savings in raw materials.

One method for lowering the production cost of glass for construction purposes is the partial or total replacement of the glass batch by cullet. This makes it possible without additional capital investments to accomplish significant savings in raw materials and to improve the ambient environment through a decrease in the pulverized emissions at the stages of preparation, dosing, mixing of material, and directly in glass melting [1, 2]. Moreover, the utilization of cullet and erclese accumulated at waste dumping grounds will free enormous areas currently occupied by industrial wastes.

The studies in [1, 2] provide data on the possibility of obtaining substantial production volumes of high-quality fluid glass in a continuous industrial glass-melting furnace, when utilizing from 30 to 100% cullet in the technological process. The experimental data and the technological recommendations offered in the above publications, as well as the positive results obtained in the analysis of service qualities of ornamental and reinforced glass, testify to the considerable promise of the research conducted in this field.

However, it was observed [1, 2] that when substantial quantities of cullet were charged into the furnace, the glass acquired an undesirable greenish shade, and the products exhibited stripes and stains of different colors, which impaired the decorative properties of the product and limited its application area (only as glazing for agricultural structures).

The purpose of the present study was to obtain bulk-tinted glass for construction purposes under the industrial conditions of large-scale production and to investigate the mechanism of glass tinting, when employing the maximum quantity of industrial glass waste.

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The studies were performed in a large continuous glass-melting furnace with a design capacity of 85 tons/day. The design parameters of the tank furnace, the type of material used, the product range, and the procedure of gradual substitution of cullet for the batch were considered earlier [1, 2]. The content of the main components in the cullet and crushed erclese used in the investigation was similar to the composition of the glass traditionally produced in the furnace (Table 1).

Table 2 gives the glass-melting temperature conditions and the position of the boundaries of the fluid glass melting zones in the tank furnace resulting from the introduction of cullet. It can be seen that the total replacement of the batch by the cullet determines the changes in the technological conditions of glass melting, molding, and the glass melting zone chart. With the traditional relationship between the batch (70%) and the cullet (30%), the position of the melting zone boundaries and the index of the degree of homogeneity of the glass melt satisfied the technological recommendations.

The monitoring of the glass melting process when using cullet instead of the batch indicated that the melting zone extended up to the end of the first pair of burners, and from there onward, the melt surface was rippled up to the barrier. The mirror-like surface was virtually nonexistent. At the same time, it was registered that most of the gas inclusions were located in the upper part of the fluid glass (100 – 150 mm) and were detained by the barrier facility immersed in the melt. The bottom layers of the glass melt which did not contain gas inclusions arrived at the cooling and molding zones. The homogeneity of the glass melt at that period was 2.5 – 3.0°C. The glass melting temperature regime was

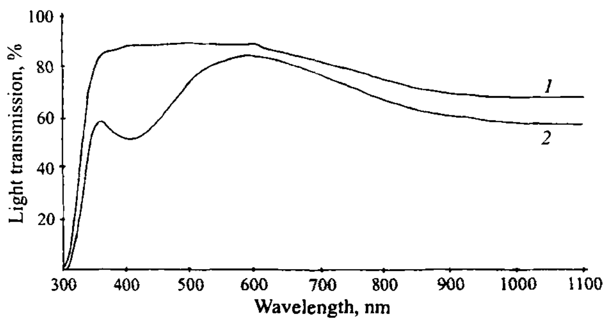

Fig. 1. Spectral curves of glass light transmission: *1*) clear glass using 30% cullet; *2*) tinted glass using 100% cullet.

changed with respect to the standard batch : cullet ratio. Due to the decrease in the diathermancy of the melt, the maximum melting temperature was brought to the upper limit permitted by the technological regulations, and the hourly fuel consumption was increased on the average by 12%. The presence of CO was registered in the gas medium above the melt (Table 2).

Table 1 shows the prescribed and the actual compositions of the glass produced in the particular system (the analyses were performed according to OST 21-67.091 – OST 21-67.12.91 standard). The study of the resulting data shows that when the batch was totally replaced by cullet of similar composition, the content of silica and oxides of alkaline and earth-alkaline metals was within the limits prescribed by the technology regulations. At the same time, a substantial variation in the content of iron oxides (increased by 51%) and sulfur (decreased by 39%) were observed. The color of the glass changed from clear glass with a greenish shade to golden brown.

In order to clarify the reasons for the increase in the iron oxide content in the glass melt, erclese crushed in a hammer crusher was subjected to chemical analysis to determine the content of the equipment iron. Its content in some samples amounted to 0.05%, which determined the increase of the Fe_2O_3 content in the glass.

The registered decrease in the SO_3 content is related to several factors. The main factors are the non-introduction of the batch (and, consequently, the absence of sodium sulfate which is part of the batch) and the increase in the melting temperature, which decreases the solubility of sulfur oxide (IV) in the melt and causes its partial volatilization in the form of SO_2 and O_2 [4].

Figure 1 shows the light transmission spectra of the clear and the tinted glass (SF-26 instrument). Both curves exhibit strong absorption bands in the violet part of the spectrum and less intense, blurred bands in the red range at a wavelength of 900 – 1100 nm. The presence of the first band is determined by the presence of the iron impurity in the form of Fe(III) in the glass. The bivalent iron is responsible for the maximum in the long-wave range, whereas the shift of the absorption band edge to the UV range of the spectrum and the increase in absorption at the wavelength of 1100 nm testify to an increase in the concentration of heterovalent forms of iron in the tinted glass composition.

The content of Fe(II) in the glasses was calculated according to the method in [5] (Table 1). In spite of the increase in the overall iron content in the tinted glass, the fraction of Fe(II) did not change and amounted to 30%. At the same

TABLE 1

Weight content of cullet in furnace charging, %	Weight content in glass, %										Diathermancy index*	Extent of glass melt homogeneity, °C	Glass
								converted to metal					
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	SO_3	Fe_2O_3	Fe(II)+ Fe(III)	Fe(II)	Fe(III)			
10 – 30 (prescribed)	72.6 ± 0.3	1.0 ± 0.2	8.7 ± 0.2	4.0 ± 0.2	13.6 ± 0.2	Up to 0.5	–	–	–	–	–	Up to 1.3	–
30	72.89	0.88	8.46	3.57	13.63	0.38	0.118	0.083	0.025	0.058	6.7	1.1 – 1.3	Clear with a greenish shade
100	72.35	1.09	8.70	3.62	13.55	0.23	0.178	0.125	0.038	0.087	5.6	2.5 – 3.0	Golden brown

* Determined according to the method in [3].

TABLE 2

Weight content of cullet in furnace charging, %	Temperature, °C		Average consumption of natural gas, nm^3/h	Volume content of CO in waste gases, %	Melting tank surface areas occupied by zones, %		
	maximum	molding			batch	foam	mirrored surface
10 – 30 (prescribed)	1500 ± 10	1200 ± 10	1200 ± 50	0,0	50		50
30	1490 – 1500	1210 – 1220	1100	0,0	15	35	50
100	1510 – 1515	1220 – 1235	1200 – 1250	0,05 – 0,20	–	100	–

time, the absolute content of Fe(II) and Fe(III) converted to metal increased by 52 and 50%, respectively, which accounts for the alteration of the glass color upon introduction of 100% cullet to the furnace.

However, the intensification of the color and the emergence of a brownish shade in the tinted glass, in our opinion, is associated as well with the formation of iron sulfide particles. This assumption is supported by the presence of the iron sulfide absorption band in the tinted glass spectral curve at a wavelength of 410 nm [4], which is absent in the glass produced by the standard technology.

The above facts testify to the redox reactions between the iron and sulfur compounds with variable valence. It is known that the equilibrium state of the considered redox reactions depends on several external factors [4]. An increase in the glass melting temperature and the presence of a weakly reducing atmosphere over the melt produce a shift in the specified equilibrium toward the formation of compounds with a lower oxidation level:

$$\mathrm{Fe(II)} \leftrightarrows \mathrm{Fe(III)};$$

$$S^{2-} \leftrightarrows SO_4^{2-}.$$

As a consequence of the above reaction, the equipment iron Fe(O) is oxidized to Fe(II) and Fe(III). The iron (the less electronegative element) tends to donate, and sulfur (the more electronegative element) to accept, electrons. The S^{2-} ion in the melt combines with part of Fe(II) and, probably, Fe(III) and forms iron sulfides which are responsible for the emergence of the absorption band near 410 nm and the golden-brown tint of the glass.

Thus, the specified results corroborate the possibility of large-scale production of building and architectural glass using industrial glass waste. The performed investigations demonstrated substantial savings in raw materials.

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